Ad-Dimer Diffusion between Trough and Dimer Row on Si(100)

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The diffusion pathways between the trough and the dimer row on the Si(100) surface are investigated by tight-binding molecular dynamics calculations using the environment-dependent tight-binding silicon potential and by *ab initio* calculations using the Car-Parrinello method. The studies discover a new diffusion pathway consisting of the rotation of the ad-dimer. The calculated energy barrier is in excellent agreement with experiment and is much more energetically favorable than other diffusion pathways by parallel and perpendicular ad-dimers. [S0031-9007(98)08071-5]

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Diffusion of Si ad-dimers on the Si(100) surface has attracted numerous experimental and theoretical investigations [1–6] because it plays an essential role in the homoepitaxial growth of silicon films. Clean Si(100) surfaces exhibit a $c(4 \times 2)$ reconstruction in which the surface Si atoms form a row of alternating buckled dimers along the [010] direction [7,8]. There are four principal ad-dimer configurations [1,5] on the Si(100) as shown in Fig. 1. An ad-dimer can sit on top of a dimer row (A and B) or in the trough between two rows (C and D), with its axis oriented either parallel (A and D) or perpendicular (B and C) to the dimer-row direction. All four configurations have been identified in scanning tunneling microscopy (STM) experiments [9]. Experimental evidence and theoretical calculations [3,6] suggest that the diffusion of ad-dimers has an anisotropic property: they prefer diffusion along the top of the dimer rows. Recently, however, using the atom tracking method [10], Borovsky *et al.* found a new mode of diffusion at 450 K [11], where the ad-dimers diffuse between the trough and the dimer row. The energy barrier for the ad-dimer to leave the trough to the top of the dimer row is estimated by the STM experiment to be 1.36 ± 0.06 eV [11]. The energy barrier for ad-dimer diffusion between the C configuration and the B configuration has been studied by Yamasaki *et al.* [6] using first-principles local density approximation (LDA) total energy calculations. They reported an energy barrier of 1.80 eV for diffusion from B to C (or 1.62 eV from C to B) which is much higher than the value observed in experiment. Neither experiment nor theoretical calculations gave the details of the diffusion pathway. In order to understand the details of diffusion pathway and clarify the discrepancy between the experiment and the theory, a careful theoretical study on the subject is highly desirable.

In this paper, we investigate the diffusion pathways and energy barriers for Si ad-dimer diffusion from the trough to the top of the dimer row using tight-binding molecular dynamics and *ab initio* total energy calculations. Because the unit cell used in such calculations contains a large number of atoms, a comprehensive search for the low energy barrier diffusion pathway is very expensive using

ab initio methods. Here we have employed tight-binding molecular dynamics calculations to explore the possible diffusion pathways and select plausible candidate pathways for study by more accurate *ab initio* calculations. Our studies reveal a new pathway which has a diffusion barrier in excellent agreement with the experimentally estimated value.

The tight-binding calculations are performed using the recently developed environment-dependent silicon tight-binding model. The model was carefully designed so that it describes well the structure and energy of the Si(100) surface, the energies of the four principal ad-dimer configurations on the Si(100), as well as the diffusion energy barriers of a single adatom on the Si(100) [12]. This model describes well the asymmetric dimer buckling on the reconstructed surface. The buckling angles are found to be 18.1°, 19.8°, and 19.9° for the $c(4 \times 2)$, $p(2 \times 2)$, and 2×1 reconstructed structures,
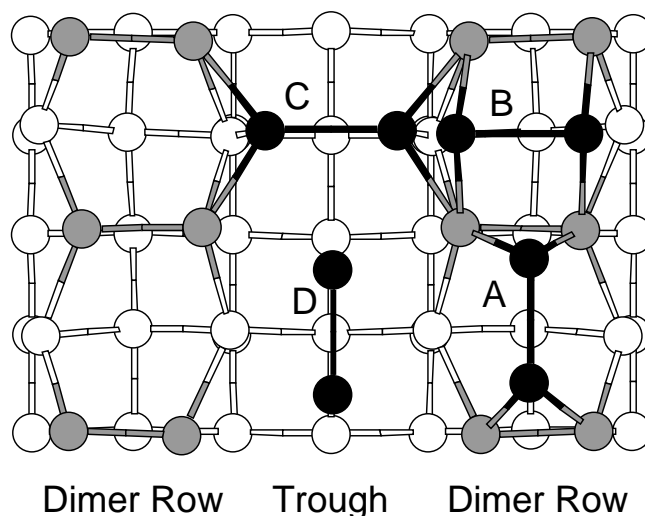

FIG. 1. Schematic drawing of the four principal dimer configurations on Si(100). The black circles represent the Si ad-dimers, the gray circles represent the dimer atoms of the Si(100) substrate, and the open circles represent the subsurface atoms.

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respectively, in good agreement with LDA results [13] of 16.9°, 18.5°, and 18.2°, respectively. The relative energies of the four principal ad-dimer configurations on the Si(100) from our tight-binding calculations are 0.0, 0.02, 0.28, and 1.02 eV, respectively, for the A, B, C, and D ad-dimer configurations on the Si(100) surface. The energies of these four ad-dimer configurations have been studied extensively by experiments and theoretical calculations. In the first-principles calculations of Brocks and Kelly [5], configuration B is placed lowest in energy, followed by A, C, and D, with relative energies of 0.0, 0.01, 0.31, and 1.11 eV, respectively. However, STM experiments [1,2] suggested that configuration B is higher in energy than configuration A by 0.059 ± 0.009 eV. Consistent with experiments, recent first-principles calculations by Yamasaki *et al.* [6] found that configuration A is indeed lowest in energy, followed by B, C, and D, with relative energies of 0.07, 0.18, and 0.76 eV, respectively. Based on the average residence time observed by STM, Borovsky *et al.* estimated that the energy difference between the dimer configurations A and C is 0.061 eV [11]. While the energy ordering is the same as the theoretical calculations, the energy difference from this experiment is smaller than that from theoretical calculations by about 0.2 eV. The energy ordering from our tight-binding calculations are in good agreement with experiment and the *ab initio* results of Yamasaki *et al.*

The calculations of the ad-dimer diffusion pathway on the Si(100) are performed using a 12-layer slab with 16 atoms per layer arranging in a 4×4 lateral unit cell. The two Si(100) surfaces are in the $c(4 \times 2)$ reconstructed structure. Ad-dimers are placed on both sides of the slab to maintain inversion symmetry. Periodic boundary conditions are applied for the directions parallel to the surface. Electronic structures are calculated using the zone center point. Structural relaxations are performed using the steepest descent method until the force on each atom is less than 0.01 eV/Å.

A straightforward pathway for ad-dimer diffusion from trough to the top of the dimer row seems to be the direct translational motion of the perpendicular ad-dimer from C to B (path I). We first calculated the energy barrier along this pathway. We move the ad-dimer along the straight line connecting the configurations C and B. For each step, the positions of all the atoms within a distance of 10.0 Å from each atom of the ad-dimer are allowed to relax. The ad-dimer atoms are also allowed to relax; the only constraint is that the coordinate of the center of mass of the ad-dimer along the diffusion direction is held fixed. The energy as the function of ad-dimer displacement along this pathway obtained by our tight-binding calculations is plotted in Fig. 2(a) (solid line). The energy barrier for the diffusion of the ad-dimer from C to B along this pathway is 1.72 eV which is much larger than the experimental value of 1.36 eV.

We have also investigated the energy barrier for the diffusion of a parallel ad-dimer from D to A. The
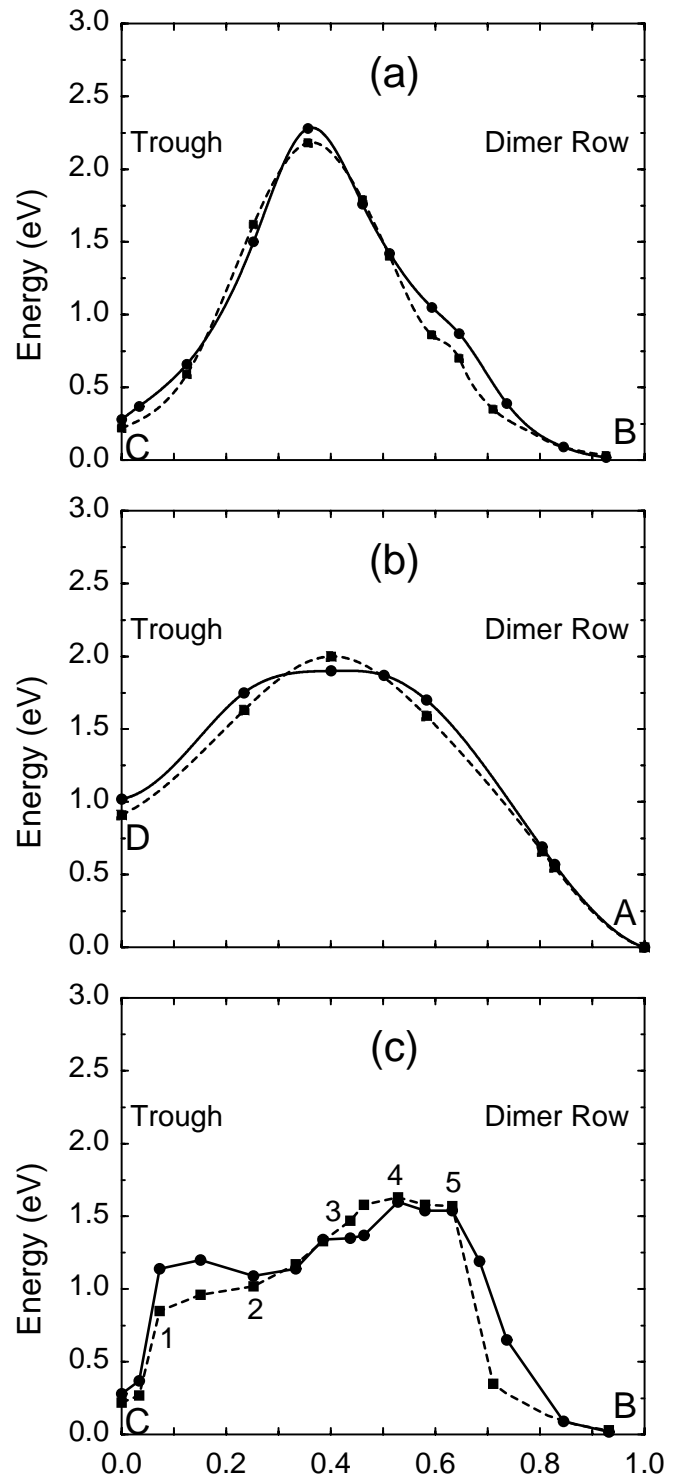

FIG. 2. The total energy variations for (a) the direct translational diffusion of a perpendicular ad-dimer (path I), (b) the direct translational diffusion of a parallel ad-dimer, and (c) the diffusion consisting of the rotation of the ad-dimer (path III). In each figure, solid lines represent the calculations by our tight-binding model, and dashed lines represent the LDA calculations. Energies are compared with respect to the energy of the dimer configuration A. The abscissa is the position of the center of the ad-dimer from the center line of the trough to the center line of the dimer row. Numbers over the points in (c) indicate geometries in Fig. 3.
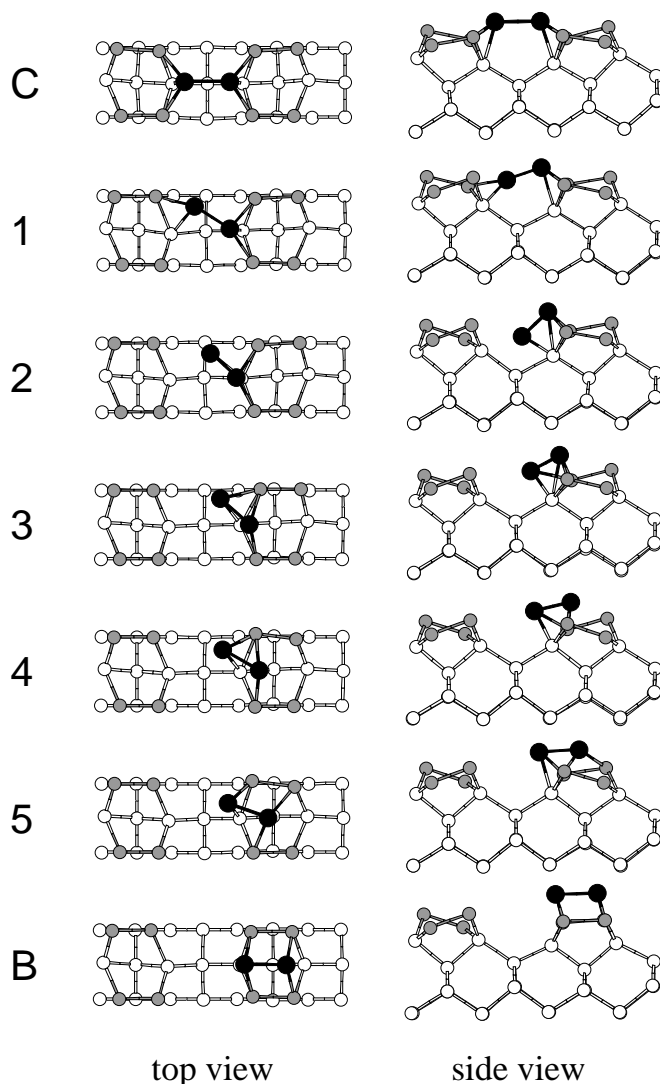
FIG. 3. Principal geometries by LDA calculations on the diffusion pathway III. The black circles represent the Si ad-dimer, the gray circles represent the dimer atoms of the Si(100) substrate, and the open circles represent the subsurface atoms. The numbering of each geometry corresponds to the number over the points in Fig. 2(c).

constraint used in this calculation is similar to that in the calculation of Fig. 2(a). The energy as a function of ad-dimer displacement for D to A along the straight pathway is plotted in Fig. 2(b) (solid line). The diffusion barrier from D to A is only 0.88 eV, which is much smaller than the experimental value of 1.36 eV. However, since the energy of the D configuration is 0.74 eV higher than that of the C configuration, the total energy barrier for diffusion from C to A via D (path II) is at least 1.62 eV which is also much higher than the experimental value.

Using tight-binding molecular dynamics as a search engine, we discovered an unusual diffusion pathway consisting of the rotation of the ad-dimer along the diffusion pathway (path III, see Fig. 3 and the discussion below) which has a diffusion energy barrier in excellent agreement with experiment. The energy along this pathway

is plotted in Fig. 2(c) (solid line). Our tight-binding calculation gives an energy barrier of 1.37 eV for ad-dimer diffusion from C to B, in excellent agreement with the experimental value of 1.36 eV.

In order to verify the results of the tight-binding calculations, we have also performed LDA calculations for the energy barriers along the three diffusion pathways as discussed above. Our calculations using the Car-Parrinello scheme [14] are performed in the framework of the density-functional theory within the LDA. Norm-conserving pseudopotentials by Stumpf et al. [15] are employed and recast into the fully nonlocal separable form as suggested by Kleinman and Bylander [16]. The exchange-correlation potential in the Ceperley-Alder form [17] as parametrized by Perdew and Zunger [18] is used. The calculations are performed using the same supercell as the tight-binding calculations and using only wave functions from the $\bar{\Gamma}$ point. The basis set contains plane waves up to an energy cutoff of 10 Ry. As one can see from Fig. 2, the results from the LDA calculations are very similar to those from the tight-binding calculations. In particular, the LDA calculations give the relative energies of 0.0, 0.03, 0.24, and 0.91 eV for the four ad-dimer configurations (A, B, C, and D), and energy barriers of 1.70 and 1.39 eV, respectively, for ad-dimer diffusion from C to B along the paths I and III suggested by the tight-binding calculations. The diffusion from C to A via D (path II) would have an energy barrier of at least 1.76 eV. The LDA calculations therefore confirm the tight-binding calculation results that path III is the most likely pathway for ad-dimer diffusion from the trough to the top of the dimer row.

Figure 3 shows the principal stages along the diffusion pathway consisting of the rotation of the ad-dimer (path III) obtained from the first-principles calculations. Stage 1 shows the rotation of one atom of the ad-dimer about the other atom. The rotating atom also goes down closer to the surface. In stage 2, the rotating atom switches bonds from atoms on one side of the trough to a subsurface atom on the other side. In stage 3, the bond between the rotating atom and the surface dimer atom on the other side of the trough is formed. The other atom of the ad-dimer remains almost stationary until stage 4 where it begins to move to the top of the dimer row. At the same time, the ad-dimer pushes the surface dimer outward, and the stress between them increases. This geometry has the highest energy in this pathway. As the ad-dimer climbs to the top of the dimer row, the total energy decreases gradually until stage 5, then decreases abruptly to a configuration very close to the final geometry B. [See the diffusion barrier curves in Fig. 2(c).]

The diffusion containing rotation is more energetically favorable than the translational diffusion of the perpendicular ad-dimer because a smaller number of broken bonds is involved along path III. For example, between stages 1 and 2 in the rotation pathway, the energy costs of breaking bonds between the rotating atom with
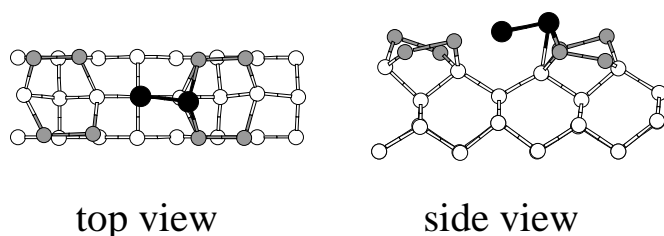
top view   side view

FIG. 4. An intermediate geometry by LDA calculations on the diffusion pathway I. This geometry corresponds to the highest energy point in Fig. 2(a).

atoms on one side of the trough is balanced by the formation of an extra bond with the subsurface atom on the other side of the trough. The energy difference between geometries 1 and 2 is only 0.17 eV. This is much lower than the intermediate stage (see Fig. 4) of the translational diffusion pathway (path I) which has more dangling bonds.

In summary, we have studied in detail the process of ad-dimer diffusion between the trough and the dimer row on the Si(100) surface by the tight-binding and *ab initio* calculations. We found that a diffusion process consisting of the rotation of the ad-dimer is more energetically favorable than diffusion processes by translation of the parallel and perpendicular ad-dimers and that our calculated diffusion barrier is in good agreement with experiment. The barrier in the diffusion pathway containing rotation is determined not simply by the breaking of bonds, but it is also affected by the stress between the ad-dimer and the surface dimers. Our silicon tight-binding model reproduces excellently the experimental observation and the first-principles calculation results for diffusion pathways by the translation of the parallel and perpendicular ad-dimers and opens up the possibility of studying surface dynamics on the Si(100) surface by using tight-binding molecular dynamics.

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